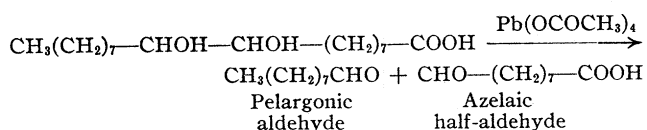


# Action of Lead Tetraacetate upon Hydroxylated Fat Acids and Related Compounds.

## I. Hydroxylated Oleic Acid, Ethyl Oleate and Oleyl Alcohol<sup>1</sup>

BY JOHN T. SCANLAN AND DANIEL SWERN<sup>2</sup>

The hydroxylation of unsaturated fat acids and related compounds and the application of the Criegee reaction to the hydroxylated products offer a means for the utilization of these materials for the production of more valuable products. The Criegee reaction<sup>3</sup> is based on the specific action of lead tetraacetate upon the  $\alpha$ -glycol group. In the reaction the bond between the two carbon atoms is broken and, depending upon the other groups attached to these carbon atoms, aldehydes or ketones are obtained. In the reactions dealt with in this investigation, two aldehydes were obtained. The reaction with 9,10-dihydroxystearic acid is typical.



Oxidation with lead tetraacetate has had very wide application in determining the structures of sugars and it has also been applied to the demonstration of the positions of the hydroxyl groups in di- and tetrahydroxystearic acids and in certain cork acids.<sup>4</sup>

Compounds suitable for the application of this reaction were prepared by hydroxylation of commercial oleic acid, ethyl oleate, and oleyl alcohol, and by the esterification of 9,10-dihydroxystearic acid. A very satisfactory method of hydroxylation with hydrogen peroxide in glacial acetic acid solution has been developed. It was suggested by a method described by Hilditch,<sup>5</sup> but includes numerous improvements. In the Hilditch method all the reactants were mixed together and allowed

to react, without application of heat, for about four to nine days, or heated on the steam-bath for several hours. The fact that the reaction is exothermic apparently escaped notice. In batches of the size used in this investigation it was found that if such a mixture is heated to about 85° and then removed from the source of heat the temperature continues to rise until the boiling point of the mixture is reached and remains there for some time. This makes temperature control difficult and high temperatures are undesirable because hydrogen peroxide is lost by decomposition and more acetylation of the product occurs. The alternative procedure at room temperature is much too slow. It was found that, if the hydrogen peroxide solution and the glacial acetic acid were mixed and heated at 85° for an hour, and then cooled to about 25° before the addition of the unsaturated compound to

be hydroxylated, the hydroxylation reaction proceeded rapidly without any application of heat and was completed in about four or five hours. The temperature of the reaction mixture never exceeded 75°. The method was further improved by greatly reducing the proportions of acetic acid and hydrogen peroxide to unsaturated compound. The method of recovering the hydroxylated product was simplified and the yields were increased.

The original Criegee method involved isolation of the lead tetraacetate after its preparation by the interaction of red lead ( $\text{Pb}_3\text{O}_4$ ) and glacial acetic acid. There is considerable advantage, however, in avoiding the separation of this unstable compound. This can be accomplished by adding red lead to a solution of the hydroxylated compound in glacial acetic acid. This variation has previously been applied in an unsuccessful attempt to prepare ketones from cholesterol<sup>6</sup> and in the preparation of acetylated alcohol from terpenes,<sup>7</sup> but has not been previously applied to the preparation of aldehydes from  $\alpha$ -glycols. The method is particularly advantageous when applied to the hydroxylation products prepared by

thoroughly with about 3000 cc. of hot water slightly acidulated with hydrochloric acid, cooled, separated from the wash water, and recrystallized from alcohol; yield, 353 g., or 45%; m. p. 89–91°; literature 95°;<sup>5</sup> neutralization equivalent, calcd. for (C<sub>18</sub>H<sub>36</sub>O<sub>4</sub>), 316; found, 316.

**Preparation of Ethyl 9,10-Dihydroxystearate.**—This compound was prepared by the esterification of 9,10-dihydroxystearic acid prepared as described above, except that the acid was used without recrystallization. The method of esterification was similar to the one described by Clarke and Davis.<sup>9</sup> After the carbon tetrachloride had been removed by distillation, the ester was separated from the residual alcoholic solution by dilution with water and recrystallized from aqueous alcohol; yield 29% (calculated on the basis of the oleic acid used for the preparation of the dihydroxy acid); m. p. 56.5–58.5°; literature 59–60°.<sup>10</sup> Saponification equivalent calcd. for (C<sub>20</sub>H<sub>40</sub>O<sub>4</sub>) 344. Found: 347.

**Preparation of 9,10-Dihydroxyoctadecanol.**—This trihydroxy alcohol was prepared by the hydroxylation of oleyl alcohol using the same molecular proportions of reactants and following the procedure described for the preparation of 9,10-dihydroxystearic acid up to the point where the product is separated by dilution of the reaction mixture with hot water. After this dilution the aqueous layer was rejected, the residual oil was neutralized with normal alcoholic potassium hydroxide and a sufficient excess of the same reagent was added to supply one mole of potassium hydroxide for each mole of oleyl alcohol.<sup>11</sup> After refluxing for two hours this solution was concentrated by evaporating most of the alcohol and the product was separated as an oil by dilution with hot water, followed by vigorous stirring. After cooling to room temperature the oil had solidified and the aqueous layer was discarded. The solid cake was remelted and then washed thoroughly with about one liter of hot water. After cooling, the solidified oil was separated from the wash water, broken up, and air-dried. When dry, the product was recrystallized from ethyl acetate after decolorization of the solution with charcoal; yield, 46%; m. p. 73–75°; literature 82–82.5°.<sup>11</sup>

**Oxidation of Purified 9,10-Dihydroxystearic Acid with Red Lead (Pb<sub>3</sub>O<sub>4</sub>) and Glacial Acetic Acid.**—A solution of 63.2 g. (0.2 mole) of 9,10-dihydroxystearic acid (prepared and recrystallized as previously described) in 500 cc. of glacial acetic acid was heated to 55–65°, and the temperature was maintained within that range while 151 g. (0.22 mole) of red lead was added in 5 to 10 g. portions through a 40-mesh sieve, with continuous stirring. Each portion was added only after the previous portion had been decolorized completely. After the last portion had been added the heating and stirring were continued until a test portion gave no green coloration when placed in contact with a few crystals of leuco-malachite green. Only a few minutes elapsed between the addition of the last portion of red lead and the completion of the reaction. The products were recovered from the reaction mixture by either of the two following methods.

**Method 1.**—The reaction mixture was diluted with 500 cc. of water and steam distilled until no more oil came over. The distillate was extracted with ether, and the ether solution was washed with water, sodium bicarbonate solution, and again with water until the washings were neutral. The ether solution was dried over calcium sulfate, and the ether was removed by evaporation under reduced pressure. The residue was a colorless oil, with a sharp but pleasant odor; yield, 20 g. or 71%. It was found to contain 94% pelargonic aldehyde as determined by the hydroxylamine hydrochloride method.<sup>12</sup> It could be further purified by vacuum distillation. The identity of this product was confirmed by preparation of the oxime, m. p. 62–63°; literature, 64°<sup>13</sup>; the 2,4-dinitrophenylhydrazone, m. p. 106–106.5°, literature 106–106.4°.<sup>4</sup> Pelargonic aldehyde is spontaneously converted to the acid on standing in contact with air. It was rapidly converted to pelargonic acid in 94% yield by air-oxidation at room temperature in the aerator described by Senseman and Stubbs.<sup>14</sup> The reaction was exothermic. The acid was purified by vacuum distillation; b. p. 142–150° (13 mm.), m. p. 11–12°; *p*-bromophenacyl ester, m. p. 64–65°, literature, 63.5°.<sup>15</sup>

The residue after the removal of the pelargonic aldehyde by steam distillation was cooled and extracted with ether. The ether solution was washed free of lead salts and acetic acid, dried over calcium sulfate, and the ether was removed by evaporation under reduced pressure. The residue, a pale yellow, viscous oil which solidified on cooling, was mainly azelaic half-aldehyde (8-formyl-1-octanoic acid); yield 22 g. or 64%. Some difficulty was experienced in the recovery and purification of this product because of polymerization. It was best purified by vacuum distillation; b. p. 195–197° (15 mm.). The purified azelaic half-aldehyde was a white solid, m. p. 40–42°; literature 38°.<sup>16</sup> Neutralization equivalent: Calcd. for (C<sub>9</sub>H<sub>16</sub>O<sub>2</sub>): 172. Found: 177. The semicarbazone, m. p. 161–162°; literature, 162°.<sup>17</sup> A sample of the crude azelaic half-aldehyde was oxidized to azelaic acid with alkaline potassium permanganate. The azelaic acid was purified by recrystallization from water; yield 25% calculated on the basis of the dihydroxystearic acid used in the first step; m. p. (and mixed melting point) 104–106°.

**Method 2.**—The reaction mixture was diluted with 500 cc. of water and extracted with two 500-cc. portions of ether. The combined ether extracts were washed with water until free from lead salts and acetic acid, dried over calcium sulfate, and the ether was removed by evaporation under reduced pressure. The pale yellow, limpid residue was chilled to about –10° and the precipitated azelaic acid (4 g.) was removed by filtration. The filtered oil was fractionated under reduced pressure with the following results: fraction (1) b. p. 35–90° (15 mm.), 4 g. (discarded); (2) b. p. 90–100° (15 mm.), 16 g., 99–100% pelargonic aldehyde, yield 57%; (3) b. p. 145–155° (15 mm.), 8 g., pelargonic acid, m. p. 11–12°; (4) b. p.

**Acknowledgment.**—The writers wish to acknowledge the advice and coöperation of Mr. P. H. Groggins of the Bureau of Agricultural Chemistry and Engineering, and of Professor Nathan L. Drake of the University of Maryland.

### Summary

1. An improved method of hydroxylating commercial oleic acid and oleyl alcohol with hydrogen peroxide in glacial acetic acid solution is described.

2. The hydroxylated products, 9,10-dihydroxystearic acid, ethyl 9,10-dihydroxystearate,

and 9,10-dihydroxyoctadecanol, have been oxidized by means of the Criegee reaction, so modified that it was not necessary to isolate the lead tetraacetate. The products obtained were pelargonic aldehyde, azelaic half-aldehyde and its ethyl ester and 9-hydroxypelargonic aldehyde.

3. It has been found that the modified Criegee reaction could be applied in some cases to the hydroxylation reaction mixture without isolating the hydroxylated products. This method was quite satisfactory for the preparation of pelargonic aldehyde from oleic acid and ethyl oleate.

WASHINGTON, D. C.